A BRIEF SURVEY OF USEFUL INFORMATION ABOUT HYDROGEN IN METALS

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INTRODUCTION

Because cold fusion phenomena are notoriously erratic, and the parameters necessary to obtain reproducible and consistent results are poorly understood, it is important to be aware of what is known about the state of hydrogen in metals and of the dynamics of its entry into and release from a metal. This short paper cannot do more than indicate some of the important areas; the interested reader can obtain more information by reading the references [1-3].

EQUILIBRIUM ASPECTS

Hydrogen dissolved in metals at low concentrations exhibits a linear relation between the concentration and the half power of the pressure, p, of the molecular gas. This is proof that hydrogen dissociates when it enters the metal. Much experimental information and theoretical considerations demonstrate that in transition metals the electron accompanying the proton of the dissociated hydrogen enters the s and d-bands of the host metal changing the density of states at the Fermi surface and causing shifts of the energy bands. The Fermi electrons concentrate about the proton, closely screening the positive charge and producing what is effectively a neutral atom [4]. These electronic reactions produce both short-range and long-range interactions between the dissolved hydrogen species.

Hydrogen occupies interstitial sites in the metal lattice, as shown by neutron diffraction in many cases. In so doing the hydrogen "atom" forces the nearest-neighbor metal atoms farther apart from each other, causing an increase of volume of the nearest-neighbor shell of atoms. The free surface of the metal specimen sweeps out to produce a larger volume increase than the volume increase of the inner shell of nearest-neighbor atoms. This is the physical reason for the increase of the lattice parameter of the metal upon absorption of hydrogen. At equilibrium a uniform distribution of dissolved hydrogen in a metal causes zero hydrostatic stress in the lattice, although each hydrogen atom is individually under a hydrostatic stress. There is no force or pressure tending to push the hydrogen atoms together into one interstitial site.

In palladium the interstitial sites having octahedral symmetry, of which there is one site per Pd atom, are the lower-energy sites so that these are preferentially occupied by hydrogen. Unlike the case with substitutional solid solutions, adding an interstitial solute atom to a metal does not increase the number of lattice sites for that solute species. The consequence is that interstitial solutes obey Fermi-Dirac statistics, and it follows that an infinitely large thermodynamic activity would result from a complete filling of all octahedral sites in a lattice. Therefore, as the molecular gas fugacity is increased in an attempt to fill all octahedral sites in palladium with hydrogen, a "spill-over" necessarily occurs into the higher-energy class of interstitial sites, namely, those of tetrahedral symmetry.

Because hydrogen changes the local and the global electronic structure of the host metal, one may expect that hydrogen changes the cohesive forces between metal atoms. Several theoretical

investigations [5] show that the cohesive interactions are in fact decreased in many transition metals including palladium. The consequence is that the effort required to cause brittle cracking of a metal is decreased by hydrogen [6]. In general, the mechanical response to applied stresses is variously affected by hydrogen in complex ways.

Dissolved hydrogen interacts attractively or repulsively with chemical and with structural singularities in the lattice. The interactions with the former, i.e., impurity atoms, are best treated from an electronic point of view. The same is true for structural imperfections when the hydrogen is exactly at the imperfection. However, at distances such that linear elasticity theory can be applied, and the stress field produced by the imperfection can be calculated, the thermodynamics of stressed bodies [7] can be used. For example, a dislocation, whether of edge, screw, or mixed type, has a stress field, as does a particle of a second phase within a matrix. The thermodynamics shows that a stress field that has a positive (i.e., tensile) hydrostatic component of stress, σ_h, decreases the chemical potential of an interstitial solute, whereas a negative hydrostatic component of stress increases the chemical potential of the solute. Therefore, at equilibrium, i.e., uniform chemical potential everywhere, dissolved hydrogen exhibits a higher concentration on the tensile side of an edge dislocation and a lower concentration on the compressive side. In cases where σ_h is zero, squared terms in the stress become significant and cause an increase in the chemical potential. Shear stresses also affect the chemical potential so that the shear stress field about a pure screw dislocation lowers the chemical potential of dissolved hydrogen. The relations between solute chemical potential and mechanical stress are valid whether the stress is internally generated, as by dislocations, second phase particles, grain boundaries, stacking faults, etc., or by externally imposed mechanical forces upon the solid body.

The appearance of one solid phase within another solid phase usually involves a change of density, and therefore stress fields are generated in the two phases which change the equilibrium compositions of the co-existing phases from those characteristic of stress-free phases. Thus, as hydrogen increases in concentration in palladium and the high-concentration phase, termed the ß-phase, is generated, the larger specific volume of the growing ß-phase causes compressive stresses upon it and a complex state of stress in the environing α-phase. Because at room temperature the Pd atoms do not diffuse and only the hydrogen atoms can move, a coherence between the α and ß lattices is maintained across the interface when the ß-particle is small. The coherent equilibrium involves equilibrium concentrations different from those obtained when the coherency is destroyed by the nuclear ion of interfacial dislocations. Thereby arises the difference between coherent and incoherent metal-hydrogen phase diagrams, and also the kinetic phenomena of hysteresis in hydrogen absorption and evolution into and from palladium.

KINETIC CONSIDERATIONS

Hydrogen has a very large mobility in transition metals especially in Pd, α-Fe, V and Nb. Its diffusivity is proportional to the product of the mobility and a thermodynamic parameter, $d \ln a / d \ln x$, where a is the thermodynamic activity and x the concentration of the hydrogen. This term can become significant at high concentrations, and in the neighborhood of the critical concentration and temperature of a miscibility gap system (of which Pd-H is an example) the thermodynamic term becomes very small.

Another reason for a decrease of the diffusivity of hydrogen in metals is the attractive interaction with chemical and structural defects. This is the so-called trapping phenomenon [8,9] which is very important at low hydrogen concentrations. Thus, dislocations in a metal will slow down the diffusion

of hydrogen when the dislocations are static. However, if the dislocations are caused to move by applied, or by internally generated shear stresses, hydrogen can be transported with the moving dislocations by virtue of the attractive interaction discussed above.

Diffusive fluxes of hydrogen are proportional to the gradient of the chemical potential of the dissolved hydrogen. Since mechanical stress affects the chemical potential, it is clear that gradients of state of stress can produce diffusive fluxes even in the absence of concentration gradients, and stress gradients can be as important, or more so, than concentration gradients for inducing diffusion of hydrogen. Temperature gradients and gradients of electrical potential can also produce fluxes of hydrogen. Lack of space prohibits discussion of these phenomena, except to assert that deductions about the state of ionicity of the dissolved hydrogen cannot be drawn from measurements of the motion of dissolved hydrogen in an electric field because of the existence of momentum transfer between electrons and electron holes and the dissolved hydrogen [10, 11].

The absorption of hydrogen into the lattice of a metal from the molecular gas must be preceded by adsorption of the molecule upon the surface, dissociation into adsorbed atoms, surface diffusion of the adsorbed atoms, and jumping of these atoms into the sub-surface region. Each of these steps is strongly affected by the atomic-scale topography of the surface and by the quantity and distribution of impurity species and any one of these steps may be kinetically controlling. If hydrogen is presented to the metal surface by electrochemical deposition or by means of a partially dissociated and/or ionized hydrogen gas, the dissociation step is avoided. In all cases the adsorbed species may encounter each other, recombine and return to the cell electrolyte as hydrogen molecules. Hence the transition of adsorbed atoms into the lattice is limited by the kinetics of the recombination reaction. To mitigate this limitation, recombination inhibitors ("poisons") may be added to the environing phase; the exact mechanisms by which these agents act are complex and not fully understood.

Further penetration from the sub-surface plane of the lattice is controlled by diffusion whose boundary condition is the sub-surface concentration, c_o, of hydrogen. This kinetically controlled concentration may be conceptually related to the input fugacity, f_i, of the source of the hydrogen: f_i equals the fugacity, f_e of molecular hydrogen gas, that at equilibrium would produce c_o in a metal at the given temperature. Sieverts law, $c_o = c = s\, f_e^{1/2}$ relates f and the hydrogen concentration, c, in the metal at equilibrium. For a gas of molecular hydrogen, there is a correlation between f_e and the gas pressure, p. However, f_i is a kinetically determined quantity without any relation to environing pressure. It is incorrect to believe that a hydrogen-charging system characterized by large f_i (because large c_o values are produced) subjects that metal lattice to a hydrostatic pressure given by the relation between p and f_e.

The input of hydrogen into the sub-surface layer expands that layer, as discussed in a previous section. Since that layer is coherent with the underlying metal which at the moment does not contain hydrogen and is therefore not expanded, a very large compressive stress is produced below the input surface; its magnitude decreases with increasing distance into the metal, and the stress becomes tensile further in. The distribution of both of the normal and the shear stresses is a function of the time of diffusion, but the largest values occur just below the input surface when the value c_o is generated there [12,13].

Because the shear stresses produced are in general very large, dislocations are generated. Some of these dislocations form entangled arrays near the input surface which increase the hardness of the metal and decrease the in-diffusion of hydrogen by trapping the atoms. Other dislocations are caused to glide, by the shear stresses, deeper into the specimen, carrying trapped hydrogen with them and

forming pile-ups at grain boundaries or being annihilated at grain and interphase boundaries. The merging of dislocations into grain boundaries causes the grain boundary to change its atomic configuration and rotation of the grains to occur with respect to each other [13]. Rotation of grains at the specimen surface can produce localized surface elevations and depressions, and emergence of edge dislocations can produce slip lines and serrations on the surface. Because of the dependence of f_i upon the atomic topography of the input surface, different metal grains achieve different c_o values and because dislocation dynamics are complicated functions of grain boundary configuration and of the orientation of the grain lattice with respect to the stress field, adjoining grains achieve different hydrogen contents at any one instant of time [13]. This phenomenon produces additional mechanical stresses between grains. This, as well as dislocation pile-ups at grain boundaries can produce microcavities the growth of which can produce linkage of the cavities and ultimately separation between grains [14]. Such separations, or cracks, fill with molecular gas at a pressure consistent with Sieverts law for the local hydrogen concentration. If the cracks communicate with the external surface of the specimen they provide channels for the loss of hydrogen from that region of the specimen [15].

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